Glass and Ceramics, Vol. 71, Nos. 1 – 2, May, 2014 (Russian Original, Nos. 1 – 2, January – February, 2014)

UDC 666.291.3

ANION-EXCHANGE SYNTHESIS OF NICKEL-CONTAINING SPINEL-TYPE PIGMENTS

G. L. Pashkov,[1, 3] S. V. Saikova,[2] M. V. Panteleeva,[1] E. V. Linok,[1, 4] and I. V. Korol'kova[1]

Translated from *Steklo i Keramika*, No. 2, pp. 19 – 22, February, 2014.

It is proposed that light-blue pigment be synthesized by co-precipitation of nickel and aluminum from nitrate solutions by the anionite AB-17-8 in OH form followed by calcination of a precursor at temperature 750°C. The product obtained is investigated by means of thermographic and x-ray diffraction analyses as well as spectrophotometry (IR and diffuse reflection). Electron microscopy shows the pigment particles to be 0.3 μm in size.

Key words: pigment, spinel, nickel, synthesis.

Coatings which are resistance to light, atmospheric and chemical actions and high temperatures are necessary for decorating articles, including ceramic articles. Ceramic pigments, which can be obtained from spinels, distinguished by resistance to high temperatures and chemical reagents, possess such properties [1, 2].

Ceramic pigments are obtained mainly by solid-phase synthesis from initial oxides, a sol-gel method or chemical co-precipitation. Solid-phase synthesis requires high calcination temperatures and prolonged comminution of powders in planetary mills. The main drawback of the sol-gel method is the time required for synthesis, since the processes occurring are based on a transition from a colloidal solution (sol) to a colloidal precipitate (gel), which occurs over a long period of time. The chemical co-precipitation method has serious advantages over the methods mentioned above for obtaining pigments because of the low synthesis temperature and high particle-size uniformity, but as a rule the precipitates obtained are contaminated with precipitator ions. At the same time the optical properties of the pigments, the most important of which for practical purposes are the color tone, brightness and saturation, are very sensitive to impurities. For this reason, the search for new ways to synthesize chemically pure pigments is becoming urgent.

Our investigations have shown that one way to solve this problem is to use organic ionites for synthesis [3 – 6]. In this case the anionite not only serves as a source of the precipitator ion OH^- but it also contains admixtures of the initial reagents and therefore does not require repeated washing and purification operations. The process can be represented by the following equation:

$$8R - HO + Ni(NO_3)_2 + 2Al(NO_3)_3 \rightarrow$$
$$8R - NO_3 + \{Ni(OH)_2 + 2Al(OH)_3\}\downarrow,$$

where $R - HO$ and $R - NO_3$ are the anionites in the OH and NO_3 forms.

In the present article we describe a method of obtaining a pigment based on nickel spinel, in which nickel and aluminum are co-precipitated from nitrate solutions with the aid of anionite in the OH form. In addition, the results obtained are compared with the results obtained with co-precipitation of nickel and aluminum by a NaOH solution.

EXPERIMENTAL PART

The strongly basic gel anionite AB-17-8 in OH form with grain size 0.25 – 0.50 mm (GOST 20302–74) was used in the present work. The procedures used to transfer the anionite into the hydroxyl form and to determine its total exchange capacity (TEC) with respect to 0.1 M hydrochloric acid are described in detail in [3].

Anion-exchange precipitation of nickel spinel (precursor) was accomplished by the following method. A weighted amount of anionite (TEC = 1.72 mmole-equiv/g) was put into contact with 0.3 M nitrate solutions of nickel and aluminum (taken in stoichiometric ratio), while mixing with a shaker for 3 h at room temperature, and passing the mixture

[1] Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Krasnoyarsk, Russia.
[2] Siberian Federal University, Krasnoyarsk, Russia (e-mail: ssai@mail.ru).
[3] E-mail: vp414@mail.ru.
[4] E-mail: vitaelin@gmail.com.

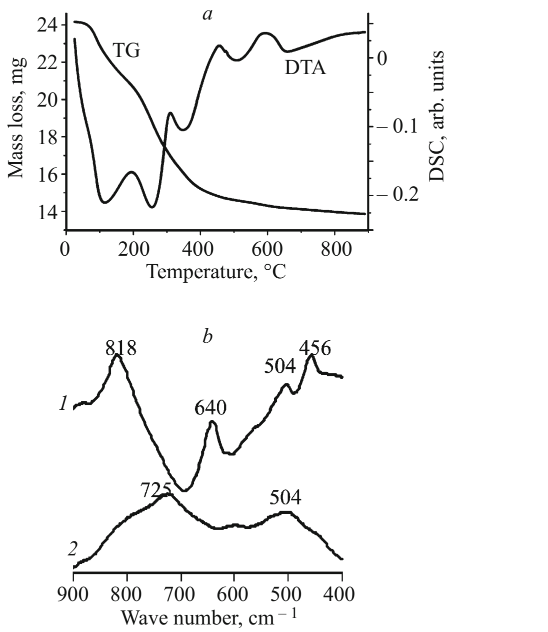

Fig. 1. Thermograms (*a*) and IR spectra (*b*) of precursors obtained by: *1*) alkali precipitation after calcination at 900°C; *2*) using an anionite after calcination at 750°C.

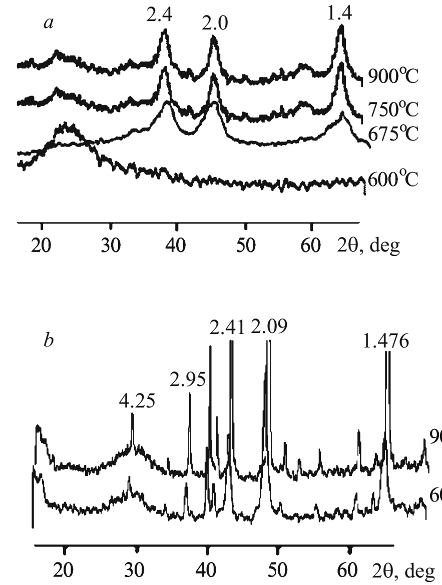

Fig. 2. X-ray diffraction spectra of the precursors obtained by using an anionite (*a*) and by alkali precipitation (*b*) at different calcination temperatures.

through a sieve with hole diameter 0.25 – 0.50 mm. The precipitate was separated by centrifuging.

For alkaline precipitation a 1 M NaOH solution was added in 50 ml drops with constant mixing in a magnetic mixer to a 0.3 M nitrate solution of nickel and aluminum (also taken in stoichiometric ratio) in 1 h. Significant excesses of the precipitator were avoided in order to eliminate the difficulties due to washing of the product.

To obtain pigment the precursors obtained were heat-treated in the interval 600 – 900°C.

The structure of the synthesized precipitates and products of calcination were identified by means of x-ray phase analysis (XPert PRO diffractometer from the PANalytical Company; CuKα radiation).

The IR absorption spectra of samples in the form of pellets with spectrally pure KBr were recorded in the frequency range 4000 – 450 cm^{-1} with a Vector 22 IR-Fourier spectrometer from the Bruker Company. The weighed portions of material and matrix were constant, and each spectrum was obtained as a result of 100 scans with resolution 2 cm^{-1}.

The particle size was determined by analyzing the precipitate in a Hitachi S-5500 scanning electron microscope with accelerating voltage 30 kV.

Thermal analysis of the precursor was performed in atmospheric air using an SDT Q600 V20.5 Build 15 apparatus (the resolution of the balance was 0.002, the resolution of the thermocouple T was 0.1°C and the resolution of DSC was 0.01 μV).

The diffuse reflection spectra in the range 200 – 800 nm were recorded in a UV-Vis-NIR Varian Cary 5000 spectrophotometer with an integrating sphere. Multistandards were used for calibration (Labsphere Spectralon diffuse color standards CSS-04-020).

DISCUSSION

The XPA data show that the precursor synthesized using an anionite to be amorphous. Thermographic analysis showed that on calcination to 900°C the change in mass of the precipitate is evidently associated with the thermal decomposition of the initial hydroxides. Several endo effects are observed in the DTA curve: at temperature 105°C — the removal of the adsorbed water; at 250°C — the removal of the interlayer water; at 360°C — the dehydroxylation of the layers and destruction of the carbonate anions, some quantity of which is present in the initial precursors because of the carbonization of the OH form of the anionite during drying in air. The effects at 515 and 600°C are probably associated with the crystallization of the product and rearrangement of its structure.

The temperature interval of calcination of the precursor (600 – 900°C) was chosen on the basis of thermographic analysis; x-ray diffraction analysis was used to investigate the products obtained (Fig. 2). The lines due to spinel $NiAl_2O_4$ appear at temperature 675°C (the diffraction peaks $\langle 2.41\rangle$, $\langle 2.00\rangle$, $\langle 1.407\rangle$) [10], but the color of the product in this case is clearly distinguished by a distinct greenish tinge, which indicates incompleteness of the spinel formation process [1]. During calcination at 750°C the color becomes characteristic for these compounds — light blue. Raising the temperature to 900°C did not change the color or the form of the x-ray diffraction pattern of the pigment (Fig. 2*a*). In the case of alkali precipitation nickel spinel is not formed even at

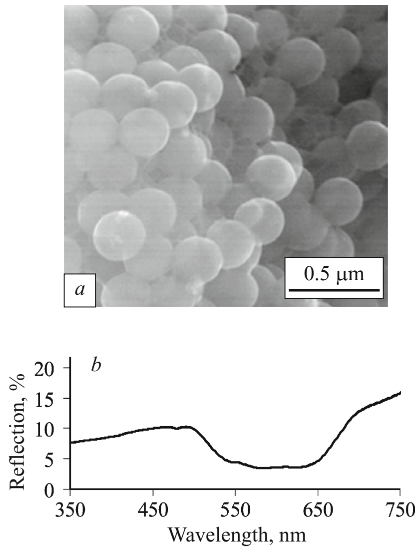

Fig. 3. Photomicrograph of the pigment $NiAl_2O_4$, obtained by anion exchange synthesis after calcination at 750°C (*a*) and its diffuse reflection spectrum (*b*).

calcination temperature 900°C. The sample consists of a mixture of nickel oxide (⟨2.08⟩, ⟨2.41⟩, ⟨2.09⟩, ⟨1.47⟩) [11], sodium aluminate (⟨4.25⟩, ⟨2.95⟩, ⟨2.66⟩) [12] and sodium nitrate (⟨3.03⟩, ⟨1.48⟩) [13]. Most likely, the presence of impurities impedes the interaction of the oxides (Fig. 2*b*).

It is evident from the analysis of the x-ray diffraction patterns that the formation of nickel spinel by anion exchange synthesis occurs at lower temperatures (750°C) than reported in the literature. For example, in [8] it is reported that $NiAl_2O_4$ was obtained at 1400°C by self-propagating high-temperature synthesis, and in the solid-phase method nickel spinel is formed at 1300°C [7].

Two maxima associated with stretching vibrations of the octahedrally and tetrahedrally coordinated aluminum are observed in the IR spectra of the pigment (see Fig. 1*b*, curve *2*) at 504 and 725 cm^{-1}, respectively, indicating the formation of reversible aluminum-nickel spinel [7, 9]. At the same time, aside from a maximum at 504 cm^{-1}, absorption bands in the region 640 – 880 cm^{-1}, due to the vibrations of tetrahedrally coordinated aluminum in sodium aluminate, are observed in the spectrum of the product of alkali precipitation (see Fig. 1*b*, curve *1*), which is in agreement with the data from x-ray phase analysis [9].

According to the scanning electron microscopy data (Fig. 3*a*) the pigment obtained by precipitation in the presence of an anionite is comprised of uniform, perfectly spherical particles of submicron size (0.3 μm). It is known that submicron size pigments promote saturation of the tone and brightness of ceramic paint [1].

Nickel spinel belongs to the class of light-blue pigments, whose color is obtained by mixing blue and green colors. The color coordinates were determined on the basis of an analysis of the diffuse reflection spectra (Fig. 3*b*) by the CIE-$L^*a^*b^*$ method [14]: $L^* = 42.31$; $a^* = –7.28$; $b^* = –18.26$. Comparing the values of the color coordinates with the data for green ($L^* = 62.49$; $a^* = –34.82$; $b^* = 16.86$) and blue ($L^* = 54.92$; $a^* = 8.04$; $b^* = –48.43$) standards attests that the color of the pigment obtained is shifted into the blue region.

Thus, a method of synthesizing nickel-containing pigment of the spinel type was developed in this work. It consists of co-precipitation of nickel and ammonia solutions by the strongly basic anionite AB-17-8 in OH form followed by calcination of the product at 750°C. The pigment obtained contains a single phase of nickel aluminate and consists of uniform spherical particles 0.3 μm in size.

Nickel-containing spinel can find application as a temperature-resistant pigment in the production of ceramic and other articles.

This work was supported in part by KGAU ‘Krasnoyarsk Krai Foundation for the Support of Scientific and Scientific-Technical Work’ and OKhNM RAN project No. 5.5.4.

REFERENCES

1. G. N. Maslennikova and I. V. Pishch, *Ceramic Pigments* [in Russian], Stroimaterialy, Moscow (2009).
2. M. A. Martynov and V. A. Vizir, *Technology for Production Ceramic Paints* [in Russian], Gostekhizdat UkrSSR, Kiev (1956).
3. G. L. Pashkov, S. V. Saikova, and M. V. Panteleeva, “Determination of the optimal conditions for ion-exchange synthesis of cobalt (II) hydroxide using AB-17-8 anionite in the OH form,” *Zh. Prikl. Khim.*, **75**(11), 1823 – 1826 (2002).
4. G. L. Pashkov, S. V. Saikova, and M. V. Panteleeva, “Anion-exchange synthesis of cobalt (II) oxalate using an anionite in C_2O_4 form,” *Zh. Sibirskogo Federal’nogo Univ., Ser. Khim.*, **2**(2), 150 – 155 (2009).
5. G. L. Pashkov, S. V. Saikova, and M. V. Panteleeva, “Anion-exchange synthesis of cobalt hydroxide,” *Khim. v Interesakh Ustoichivogo Razvitiya*, No. 9, 57 – 60 (2001).
6. G. L. Pashkov, S. V. Saikova, M. V. Panteleeva, et al., “Anion Exchange Synthesis of Spinel-Type Cobalt-Containing Pigments,” *Steklo Keram*., No. 6, 28 – 31 (2013); G. L. Pashkov, S. V. Saikova, M. V. Panteleeva, et al., “Anion Exchange Synthesis of Spinel-Type Cobalt-Containing Pigments,” *Glass Ceram*., **70**(5 – 6), 225 – 228 (2013).
7. Y. S. Han, J. B. Li, X. S. Ning, et al. “Study on NiO excess in preparing $NiAl_2O_4$,” *J. Mater. Sci. Eng.*, **369**(1 – 2), 241 – 244 (2004).
8. A. Yu. Chapskaya, *Production of Ceramic Pigments based on Spinel by Self-Propagating High-Temperature Synthesis, Author’s Abstract of Candidate’s Thesis* [in Russian], Tomsk (2007).
9. P. Jeevanandam, “Preparation of nanosized nickel aluminate spinel by a sonochemical method,” *J. Mater. Sci. Eng.*, **90**, 125 – 135 (2002).
10. *Powder Diffraction File*, JCPDS 10–339
11. *Powder Diffraction File*, JCPDS 47–1049.
12. *Powder Diffraction File*, JCPDS 19–1179.
13. *Powder Diffraction File*, JCPDS 7–271.
14. D. Visinescu, F. Papa, A. Ianculescu, et al., “Nickel-doped zinc aluminate oxides: starch-assisted synthesis, structural, optical properties, and their catalytic activity in oxidative coupling of methane,” *J. Nanopart. Res*., **13**, 1456 – 1470 (2013).